

Narrowband fluorescent nanodiamonds produced from chemical vapor deposition films

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We report on the production of nanodiamonds (NDs) with 70-80 nm size via bead assisted sonic disintegration (BASD) of a polycrystalline chemical vapor deposition (CVD) film. The high crystalline quality NDs display intense narrowband (7 nm) room temperature luminescence at 738 nm from in situ incorporated silicon vacancy (SiV) centers. We demonstrate bright, narrowband single photon emission with > 100000 cps. Due to the narrow fluorescence bandwidth as well as the near-infrared emission these NDs are also suitable as fluorescence labels with significantly enhanced performance for in-vivo imaging.

In recent years fluorescent nanodiamonds (NDs) have attracted increasing attention in a wide field of prospective applications e.g. fluorescence labeling in biological imaging¹⁻³ and as solid-state single photon sources (SPSs)⁴. In these applications they stand out owing to photostable fluorescence¹, bio compatibility² and feasible surface functionalization³. The majority of the experiments performed in these fields rely on the fluorescence of the nitrogen vacancy (NV) center in diamond. NV centers are readily available as single centers in NDs⁵ or created by irradiating diamond powders^{1,4}. Recent work also demonstrated the efficient production of NV containing NDs by ball milling of microcrystalline powder⁶. Despite these advantages, NV centers exhibit two major drawbacks for the applications mentioned above: their room temperature fluorescence spectrum spans about 100 nm⁵ and, due to their zero-phonon-line (ZPL) at 637 nm, excitation with visible laser light (typ. at 532 nm) is necessary. On the other hand, the silicon vacancy (SiV) center delivers superior fluorescence properties. Firstly, it exhibits a ZPL at ≈ 738 nm⁷⁻⁹, lying within the near-infrared window of biological tissue¹⁰. Furthermore, due to low electron-phonon-coupling about 80 % of the fluorescence is emitted into the ZPL even at room temperature^{11,12} with an ensemble width of only 5-6.6 nm^{7,8}. These properties lead to exceptional advantages in the potential applications of SiV-containing NDs: Firstly, the fluorescence can be excited using red laser light (here: 671 nm) thereby minimizing tissue autofluorescence for in-vivo imaging applications^{1,10}. Simultaneously, absorption of the excitation laser is ≈ 20 times lower compared to 532 nm¹⁰, thus enabling imaging of deep tissue which is crucial for life science applications. Secondly, the significantly reduced fluorescence bandwidth allows for narrow spectral filtering, even fur-

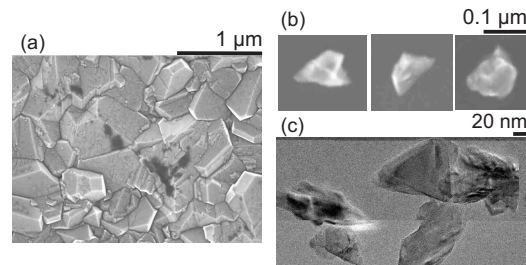


FIG. 1. SEM Images of: (a) the polycrystalline starting material, (b) individual NDs after spin coating onto a Si substrate. (c) High resolution transmission electron microscopy (HR-TEM) images of dropcast colloid on a copper grid with lacey carbon film.

ther reducing autofluorescence in imaging applications. The narrow-band fluorescence also enables efficient discrimination of single photon emission and background signals for applications in e.g. quantum cryptography. As we show in this work, the SiV centers emit in a spectral region where background emission from the diamond material is low. Combined with the enhanced photon extraction from NDs⁴ SiV centers in NDs thus are promising candidates for practical solid state SPSs.

Commonly, SiV centers are observed in all types of chemical vapor deposition (CVD) diamonds including homoepitaxial single-crystalline⁹ and polycrystalline materials⁷ due to Si incorporation by etching of Si substrates and CVD reactor walls. These SiV centers produced in situ during CVD growth seem to possess superior fluorescence properties as compared to SiV centers produced by ion implantation: the latter ones were examined as SPSs⁸ but showed unfavorably low emission rates (1000 counts per second (cps)). On the other hand, single SiV centers produced in situ in CVD grown NDs demonstrated very bright emission with 10^6 cps recently¹². These substrate bound CVD NDs, however, are not applicable as fluorescence labels requiring NDs in solution or for enhanced SPSs which require spatial nanomanipulation to achieve coupling to photonic or nanoplasmonic

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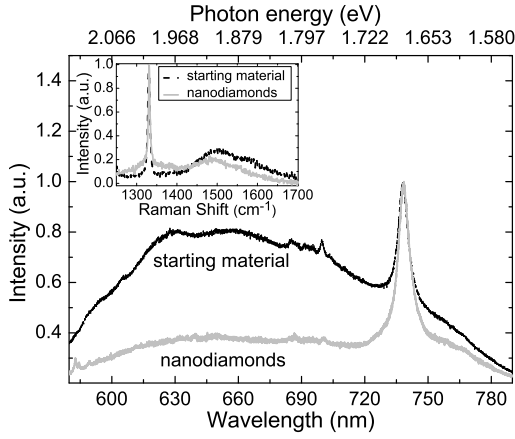


FIG. 2. Photoluminescence spectra recorded under 532 nm laser excitation from the polycrystalline starting material and an ensemble of the produced NDs. The inset shows the Raman spectrum of the starting material and the NDs recorded with 488 nm laser light.

structures⁵. We here report the production of fluorescent NDs containing in situ produced SiV centers from polycrystalline CVD films via the bead assisted sonic disintegration (BASD) method. These NDs combine the advantageous SiV fluorescence properties and its feasible production during the CVD process with the extended applicability of NDs dispersed in solution.

As starting material for ND production we employ a polycrystalline diamond film grown by rho-BeSt Coating GmbH (Innsbruck) using hot filament CVD on ND seeded Si¹³. Scanning electron microscope (SEM) images indicate a film thickness of 2 μm and high crystalline quality (grain size 0.5-1 μm , Fig. 1(a)). Raman spectroscopy reveals a distinct diamond Raman line (1330.3 cm^{-1} , inset Fig. 2); its width of 5.9 cm^{-1} indicates high crystalline quality with moderate stress distribution¹¹. A weak G-band at around 1510 cm^{-1} is attributed to residual sp^2 carbon. The film thus provides a high quality starting material for ND production. Photoluminescence measurements (Fig. 2) display a pronounced SiV ZPL at 738.2 nm (width 5.6 nm in accordance with the literature^{7,8}). Additionally, we observe a broad band fluorescence that strongly diminishes beyond 700 nm¹³. The characterized diamond film is used for ND production after removing the substrate by chemical etching.

The BASD process, that some of us disclosed recently^{14,15}, enables the deagglomeration of strongly agglomerated nanoparticles by charging ceramic microbeads to a sonicated suspension. The microjets or shock waves induced by ultrasonic cavitations propel the beads (here: ZrO_2 , 50 μm size) leading to the disintegration of large agglomerates and the eventual formation of colloidal solutions of primary nanoparticles. So far, the method has only been applied for the deagglomeration of nanoparticles bound by inter-particle forces. Here, we

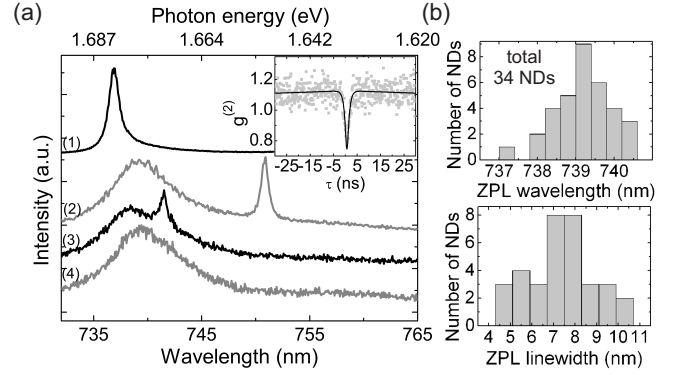


FIG. 3. (a) Photoluminescence spectra of individual NDs. Inset: $g^{(2)}$ function of ND (1), fit taking into account background and instrument response revealing $g^{(2)}(0) \approx 0.05$, (b) Histogram of ZPL positions and widths (mean value 6.8 nm).

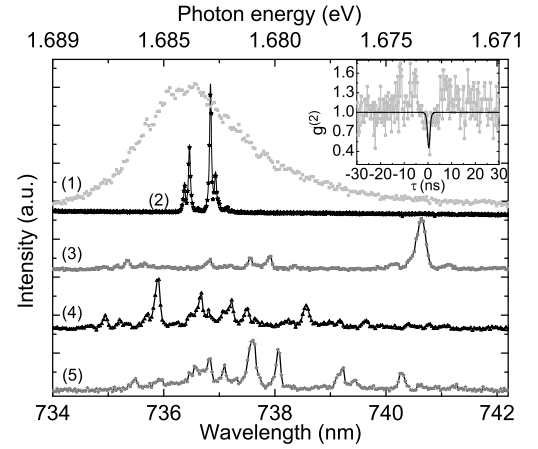


FIG. 4. Photoluminescence spectra at cryogenic temperatures. (1) SiV luminescence from 1.65 μm thick polycrystalline film at 4.7 K, (2) SiV luminescence from high quality 100 nm thick homoepitaxial film at 23.5 K, (3)-(5) spectra of individual NDs at 30 K, Inset: $g^{(2)}$ function of ND (3)

apply the BASD technique as a top down approach for the production of nanoparticles from a CVD diamond film by separating the grains and crushing the μm -sized crystals. The BASD process is followed by several purification steps¹³, delivering a colloidal suspension of NDs in deionized water. The average particle size, determined by dynamic light scattering directly in the resulting solution, shows a distribution maximum at 70-80 nm¹³. As the cumulative size distribution shows that more than 80 % of all particles have a size <100 nm¹³, these NDs are highly suitable for in-vivo imaging applications². HRTEM and SEM observation verified the diamond nature of the nanoparticles as well as the nanometric size (Fig. 1(b)\(c\)). The faceted shape of the individual NDs indicates the crushing of the film's crystallites along lattice planes. No contamination from the BASD process was found in the final colloidal solution¹³.

To determine the fluorescence properties the ND solu-

tion is diluted and spin coated onto Si or Ir substrates. In a first step, we investigate a large ensemble of NDs on a sample with high density. Raman measurements certify conservation of the crystalline quality throughout the production process (Raman line 1331.2 cm^{-1} , width 5.1 cm^{-1} , inset Fig. 2). Thus, the NDs provide high crystalline quality hosts for SiV centers, indispensable for achieving bright SiV luminescence¹². Fig. 2 displays a typical fluorescence spectrum of a ND ensemble. We achieve significant reduction of broadband fluorescence, while the SiV luminescence remains basically unchanged (ZPL 738.6 nm , width 6.8 nm). The reduced background is very promising with respect to applications of the NDs as solid state SPSs.

To perform single ND spectroscopy on a low density sample we use a homebuilt confocal microscope setup¹² (NA 0.8, excitation $660/671 \text{ nm}$). The spectra of four individual NDs are shown in Fig. 3(a), displaying intense SiV ZPLs. A histogram of the observed line positions is given in Fig. 3(b), displaying peak wavelengths between 737.4 nm and 740.3 nm . The 'ensemble ZPL' widths of 3.8 to 9.9 nm confirm narrowband luminescence for all NDs investigated. The spread of the line positions and widths is caused by varying stress in the NDs^{11,12}. We perform polarization dependent excitation studies, yielding up to 50 % visibility, evidencing (partial) alignment of the color centers inside the NDs. We point out that the observed fluorescence was photostable under excitation with up to $\approx 1000 \text{ kW/cm}^2$. The measured ensemble fluorescence rates did not saturate, partially exceeding the maximum count rate of our photon counters (10^7 cps). Therefore, the NDs containing larger ensembles of SiV centers are applicable as bright, narrowband, photostable fluorescence labels.

In addition to these ensemble ZPLs we observe lines as narrow as 0.8 nm (see Fig. 3(a),(1)-(3)). Comparable line widths have been recently reported for single SiV centers¹², thus we tentatively attribute these lines to shifted, bright single SiV centers. We find that some of the NDs (Fig. 3(a),(1)) show dominant bright emission ($> 100000 \text{ cps}$) from a single SiV center, verified by nonclassical intensity autocorrelation ($g^{(2)}$ -)measurements^{4,12} (Fig. 3(a) inset). We thus demonstrate a SiV based SPS from a colloidal ND solution featuring a ZPL linewidth of $\approx 1.5 \text{ nm}$ at room temperature.

To gain further insight into the ND fluorescence we perform low temperature ($4.7 - 30 \text{ K}$) spectroscopy. Fig. 4 displays luminescence spectra from individual NDs, a high quality homoepitaxial and a polycrystalline CVD film. The observed lines blue-shift as compared to the room temperature ZPL in agreement with the literature⁷. The spectrum of the homoepitaxial film displays a four line fine structure indicating a split excited and ground state⁹, while this structure is washed out in the polycrystalline film due to inhomogeneous broadening. The spectra of the NDs also show a fine structure (individual line widths 0.1 nm), but are more complex due to

sub-ensembles of SiV centers under different stress, corresponding to the broadening in the polycrystalline film. Again some of the NDs show dominant emission from a single SiV center (Fig. 4 inset), evidencing low temperature single photon emission.

In summary we have demonstrated that BASD of diamond films produces fluorescent NDs that preserve or even enhance favorable properties of the starting material i.e. high brightness, narrowband fluorescence, low background emission and high photostability. We demonstrate bright ($> 100000 \text{ cps}$) single photon emission from SiV centers at room temperature. The fluorescent NDs also offer great potential as optimized fluorescence labels, where additional Si doping could further enhance the performance. For single photon applications, smaller NDs produced from purer diamond material are desirable. As the method presented here is easily scalable it pioneers the production of large amounts of NDs with engineered defect properties from a variety of diamond films.

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Supplementary material for: Narrowband fluorescent nanodiamonds produced from chemical vapor deposition films

The supplementary material covers details of the BASD process, including the employed purification steps, as well as the data of the nanodiamond (ND) size measurements by dynamic light scattering (DLS). We give additional information on the luminescence spectra discussed in the paper.

Additional discussion on fluorescence spectra and starting material:

The polycrystalline diamond film used as a starting material has been grown by rho-BeSt using a hot filament CVD Process. As substrate a 4" ND seeded {100}-oriented Si wafer has been used. The growth was performed using 0.26 % CH₄ in H₂. Taking into account the SEM images, the film provided approx. 0.053 g of diamond material.

In Fig. 5 (cf. Fig 2, original manuscript) additional lines between 680 and 705 nm are observed in the fluorescence spectrum. As these lines are not relevant for the SiV re-

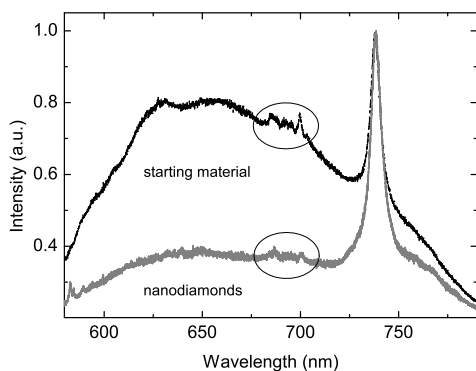


FIG. 5. Photoluminescence spectra recorded under 532 nm laser excitation from the polycrystalline starting material and an ensemble of the produced NDs. The marked areas show the tantalum related lines.

lated topics they are not discussed in the paper. This triplet has been tentatively attributed to the incorporation of tantalum from the hot filament process¹⁶. As these fluorescence lines are rather weak and nearly coincide with the maximum of the broad fluorescence background observed, the application of these centers as fluorescence markers or single photon sources is unfavorable.

Additional information on the BASD process:

As described in the manuscript we apply a BASD process to crush a polycrystalline diamond film. So far, the method has only been applied for the deagglomeration of nanoparticles bound by inter-particle forces (electrostatic, π - π interactions, hydrogen bonding, bonds be-

tween surface groups). Here, the BASD technique has been applied for the production of nanoparticles from a CVD diamond film, as these films are not easily processed in a conventional grinding tool such as a mortar or ball mill due to technological restrictions (available amounts

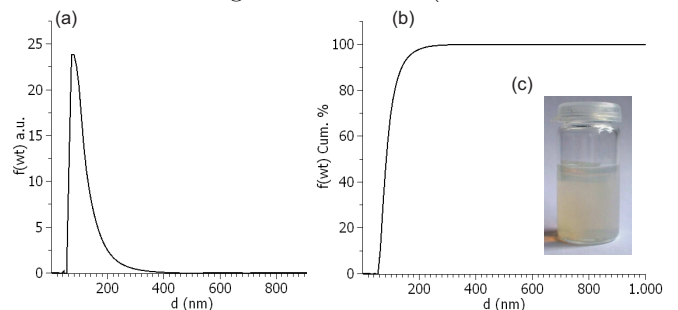


FIG. 6. (a) size distribution of the ND colloid, (b) cumulative size distribution of the colloidal solution. (c) ND colloid in deionized water obtained from a BASD-treated CVD diamond film

of starting material, applicable forces, necessity to crush the crystallites along crystal planes etc.). In preliminary experiments to this study we observed that beadless ultrasonic treatment was not effective for the crushing of diamond films. Therefore, the BASD process and the following purification have been carried out: Sheets of the diamond film and ZrO₂ microbeads (50 μ m) were treated in 5 ml of dimethyl sulfoxide (DMSO) for 2 h using a powerful sonotrode (400 W) equipped with a horn-type sonotrode. 200 ml of toluene were added to the reaction mixture. The sediments were separated by centrifugation and washed with 100 ml of acetone. In order to remove impurities like sonotrode abrasion, amorphous carbon and nanozirconia fragments, the residue was first stirred overnight in a 1:1:1 mixture of conc. H₂SO₄, HNO₃ and HClO₄ at 85 °C. Secondly, the zirconia beads have been removed by centrifugations. The resulting supernatant was then stirred in 20 N KOH overnight and centrifuged. The sediment was washed in repeated centrifugation-redispersion cycles with deionized water until pH 7 and stored as a colloidal solution (Fig. 6(c)) in deionized water. The average particle size, i.e. hydrodynamic diameter determined by dynamic light scattering (DLS) directly in the colloidal solution of the resulting ND particles, is well below 100 nm with the distribution maximum at 70-80 nm (Fig. 6(a)). The cumulative size distribution shows that more than 80 % of all particles have a size < 100 nm (Fig. 6(b)). EDX measurements after the purification proved the absence of zirconia contamination.